Synthesis of 1,3-thioxoketones from salicylaldehyde*

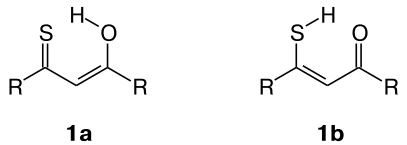
*I. S. Semenova,[a] V. N. Yarovenko,[a] K. S. Levchenko,[b] and M. M. Krayushkin[a]**

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. E-mail: mkray@ioc.ac.ru; irisemyonova@gmail.ru*
[b]*Central Research Technological Institute "Tekhnomash", 4 ul. Ivana Franko, 121108 Moscow, Russian Federation*

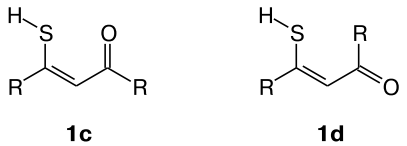
A method for the synthesis of monothiodibenzoylmethanes was developed. The method involves a reaction of potassium thioacetate with 1-(2-hydroxyphenyl)-3-phenylpropynone prepared from salicylaldehyde.

Key words: 1,3-thioxoketones, chelates, chromones, propynones, tautomers.

Interest in 1,3-thioxoketones is due to their structural features (they can exist as four tautomers **1a—d** (see Refs 1—4)) and good chelating properties.

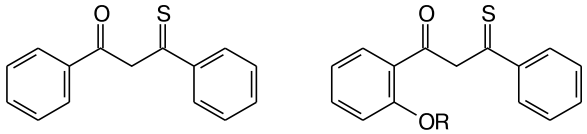


1a **1b**



1c **1d**

For instance, metal complexes with monothiodibenzoylmethane **2** have been reported.[5—7]



2 **3**

It is clear that their properties will largely depend on *ortho*-substituents of the aromatic rings. However, compounds of the type **3** are not documented, probably because the most obvious synthetic routes to these derivatives are complicated by possible cyclization into the chromone system involving the hydroxy or ether group.

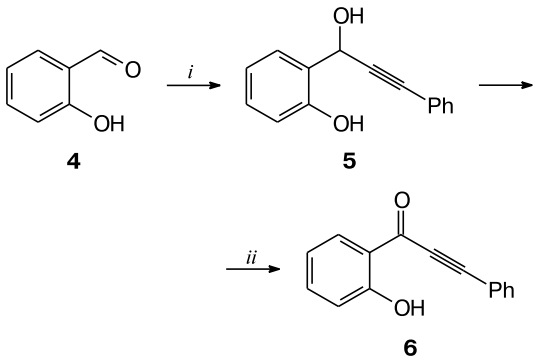
In the present work, we propose a method for the synthesis of monothiodibenzoylmethanes **3** containing an ether group in the *ortho*-position.

Our experiments showed that 2-hydroxyacetophenone does not react with ethyl benzenecarbodithioate in the presence of NaH or Bu^tOK.

An alternative way in which we tried to construct a thioxo group involved replacement of vinylic halogens in chalcones.

To do this, we used salicylaldehyde **4** in a reaction with phenylacetylene to give propargyl alcohol **5**, which then was oxidized with MnO_2 into phenylpropynone **6** (Scheme 1).

Scheme 1



i. 1) BuLi, THF, −78 °C; 2) HC≡CPh; *ii.* MnO_2, CH_2Cl_2.

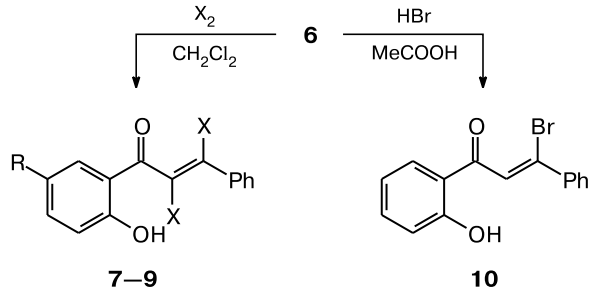
Reactions of phenylpropynone **6** with halogens afford di- and trihalides **7—9** (Scheme 2). Monobromide **10** was obtained by a reaction of HBr with compound **6** in acetic acid.

However, it turned out that compounds **7—9** readily undergo base- or acid-catalyzed cyclization into the corresponding 2-phenylchromones **11—13**. For instance, compounds **7** and **8** yield dibromochromone **11** and

* Dedicated to Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1021—1024, April, 2013.

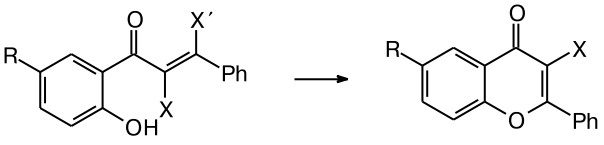
Scheme 2



R = X = Br (**7**); R = H, X = Br (**8**); R = H, X = I (**9**)

bromochromone **12**, respectively. Treatment of compounds **9** and **10** with K_2CO_3 in DMF gave 2-phenylchromone **13** (Scheme 3). Obviously, this strategy is unsuitable for subsequent functionalization of compounds **7**—**10** *via* nucleophilic substitution of a mercapto group for the Br atom.

Scheme 3

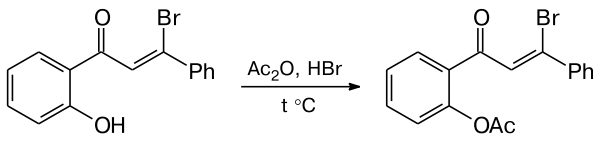


7—10 **11—13**

Compound	R	X	X′	Compound	R	X
7	Br	Br	Br	**11**	Br	Br
8	H	Br	Br	**12**	H	Br
9	H	I	I	**13**	H	H
10	H	H	Br			

To prevent possible cyclization, we protected the OH group in monobromide **10** by its conversion into acetate **14** (Scheme 4). The reaction was successfully carried out in acetic anhydride in the presence of HBr; with H_2SO_4 as a catalyst, a complex mixture of products was formed.

Scheme 4

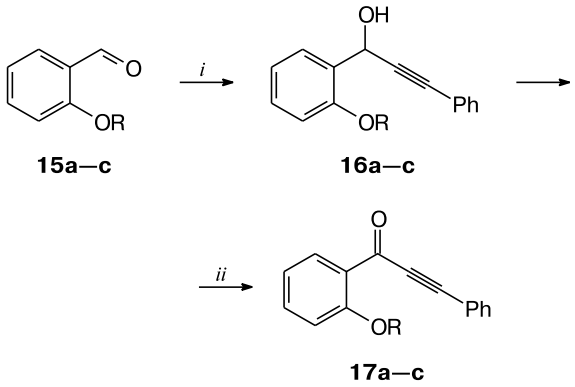


10 **14**

Attempted replacement of the Br atom in compound **14** by using Na_2S in DMF, NaHS in DMF, and potassium thioacetate failed: the reaction always produced chromone **13**.

This failure prompted us to provide more stable protection to the OH group under these reaction conditions. For this purpose, starting from salicylaldehydes **15a**—**c** with the OH group protected by methyl, benzyl, and *tert*-butyl(dimethyl)silyl groups, we obtained the corresponding phenylpropynones **17a**—**c** (Scheme 5).

Scheme 5



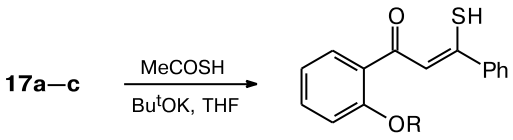
15a—c **16a—c** **17a—c**

17: R = Me (**a**), $PhCH_2$ (**b**), Bu^tMe_2Si (**c**)

i. 1) BuLi, THF, –78 °C; 2) HC≡CPh; *ii*. MnO_2, CH_2Cl_2.

Indeed, we found that reactions of ethers **17a**—**c** with potassium thioacetate (Scheme 6) give earlier unknown monothiodiketones **18a**—**c** containing an ether group in the *ortho*-position.

Scheme 6



18a—c

18: R = Me (**a**), $PhCH_2$ (**b**), Bu^tMe_2Si (**c**)

The structures and chelating properties of the β-thioxoketones obtained will be described elsewhere.

Experimental

^{1}H NMR spectra were recorded on Bruker AC-200 (200 MHz) and Bruker AM-300 instruments (300 MHz) in $CDCl_3$. ^{13}C NMR spectra were recorded on Bruker AM-300 (75 MHz) and Bruker AC-200 instruments (50 MHz) in $CDCl_3$. The carbon atom and residual protons of the solvent served as the internal standard. Mass spectra were measured on a Varian MAT CH-6 instrument (direct inlet probe, ionizing energy 70 eV, control voltage 1.75 kV). Melting points were determined on a Boetius hot stage and are given uncorrected. All the reaction mixtures were analyzed and the purity of the products obtained were checked by TLC on Silica gel 60 F254 UV-254 plates (Merck).

Synthesis of phenylprop-2-yn-1-ols (general procedure). A 2.2 *M* solution of BuLi (1.2 equiv.) in hexane was slowly added

at −78 °C to a solution of freshly distilled phenylacetylene (1.2 equiv.) in dry THF. The reaction mixture was warmed to −40 °C, stirred for 10 min, and cooled again to −78 °C. A solution of dry salicylaldehyde (or its O-substituted analogs **15a—c**) (1 equiv.) in THF was slowly infused through a syringe. The reaction mixture was stirred at −78 °C for 4.5 h and neutralized with a saturated solution of NH_4Cl. The tetrahydrofuran was removed from the aqueous solution under reduced pressure. The product was extracted with ethyl acetate. The combined organic fractions were washed with brine, dried with anhydrous Na_2SO_4, and concentrated. The resulting solid or oil was purified by flash chromatography.

1-(2-Hydroxyphenyl)-3-phenylprop-2-yn-1-ol (5). Yield 76%, m.p. 87—88 °C (*cf.* Refs 8, 9: m.p. 88 °C).

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (16a).[10] Yield 2.23 g (70%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 7.68 (dd, 1 H, J = 7.5 Hz, J = 1.3 Hz); 7.46—7.55 (m, 2 H); 7.29—7.41 (m, 4 H); 7.03 (t, 1 H, J = 7.5 Hz); 6.95 (d, 1 H, J = 8.2 Hz); 5.97 (d, 1 H, J = 5.9 Hz); 3.92 (s, 3 H); 3.21 (d, 1 H, OH, J = 5.9 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$), δ: 156.8, 131.7 (2 C); 129.6, 128.3, 128.2, 128.1 (2 C); 127.9, 122.7, 120.8, 110.9, 88.5, 85.9, 61.4, 55.5. MS, m/z (I_{rel} (%)): 238 $[M]^+$ (30), 222 $[M - OH]^+$ (100), 207 $[M - OMe]^+$ (37).

1-(2-Benzyloxyphenyl)-3-phenylprop-2-yn-1-ol (16b). Yield 3.56 g (96%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 7.72 (dd, 1 H, J = 7.5 Hz, J = 1.2 Hz); 7.50—7.62 (m, 4 H); 7.31—7.42 (m, 7 H); 7.07 (t, 1 H, J = 7.5 Hz); 7.01 (d, 1 H, J = 8.4 Hz); 6.02 (s, 1 H); 5.21 (s, 2 H); 3.32 (s, 1 H, OH). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 155.9, 136.6, 131.7 (2 C); 129.5, 129.3, 128.6 (2 C); 128.3, 128.2, 128.0 (3 C); 127.2 (2 C); 122.8, 121.1, 112.2, 88.8, 85.7, 70.2, 61.8. MS, m/z (I_{rel} (%)): 314 $[M]^+$ (21), 297 $[M - OH]^+$ (28), 223 $[M - PhCH_2]^+$ (74), 205 $[M - PhCH_2O]^+$ (80), 91 $[PhCH_2]^+$ (100).

1-[2-(*tert*-Butyldimethylsilyloxy)phenyl]-3-phenylprop-2-yn-1-ol (16c). Yield 2.55 g (89%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 7.71 (d, 1 H, J = 7.6 Hz); 7.46—7.53 (m, 2 H); 7.30—7.38 (m, 3 H); 7.26 (t, 1 H, J = 7.7 Hz); 7.04 (t, 1 H, J = 7.5 Hz); 6.91 (d, 1 H, J = 8.1 Hz); 5.98 (m, 1 H); 2.94 (s, 1 H, OH); 1.09 (s, 9 H); 0.34 (s, 6 H). ^{13}C NMR (75.45 MHz, $CDCl_3$), δ: 152.9, 131.6 (2 C); 131.1, 129.3, 128.29, 128.1 (2 C); 128.0, 122.7, 121.4, 118.4, 88.8, 85.9, 61.2, 25.7 (3 C); 18.2, −4.1 (2 C). MS, m/z (I_{rel} (%)): 338 $[M]^+$ (2), 281 $[M - Bu^t]^+$ (91), 251 $[M - Bu^t - 2\ Me]^+$ (100), 224 $[M - C_6H_{14}Si]^+$ (8), 201 $[M - C_6H_{14}SiO]^+$ (12).

Oxidation of phenylprop-2-yn-1-ols (general procedure). Manganese dioxide (4.3 g) was added in portions to a solution of phenylprop-2-yn-1-ol **5** or its derivatives **16a—c** (8.45 mmol) in dry CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature until the reaction was completed (monitoring by TLC). Manganese oxide was filtered off, and the resulting solution was concentrated. The product was purified by flash chromatography.

1-(2-Hydroxyphenyl)-3-phenylprop-2-yn-1-one (6). Yield 65%, m.p. 66 °C (*cf.* Refs 8, 9: m.p. 65 °C).

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-one (17a).[10] Yield 2.17 g (96%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 8.18 (d, 1 H, J = 7.7 Hz); 7.62 (d, 2 H, J = 7.2 Hz); 7.53 (t, 1 H, J = 7.8 Hz); 7.35—7.44 (m, 3 H); 7.00—7.08 (m, 2 H); 3.95 (s, 3 H). ^{13}C NMR (75.45 MHz, $CDCl_3$), δ: 176.5, 159.7, 134.9, 132.8 (2 C); 132.4, 130.3, 128.5 (2 C); 126.7, 120.6, 120.2, 112.2, 91.4, 89.2, 55.8. MS, m/z (I_{rel} (%)): 236 $[M]^+$ (92), 219 $[M - OH]^+$ (11), 207 $[M - OMe]^+$ (85), 129 $[M - C_7H_7O]^+$ (95), 115 (100).

1-(2-Benzyloxyphenyl)-3-phenylprop-2-yn-1-one (17b). Yield 3.42 g (97%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 8.19 (d, 1 H, J = 8.0 Hz); 7.49—7.59 (m, 3 H); 7.38—7.48 (m, 3 H); 7.27—7.38 (m, 5 H); 7.05—7.11 (m, 2 H); 5.23 (s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 176.4, 158.7, 136.2, 134.8, 132.7 (2 C); 132.0, 130.2, 128.5 (2 C); 128.4 (2 C); 127.8, 127.3, 127.1 (2 C); 120.6, 120.5, 113.5, 91.8, 89.5, 70.6. MS, m/z (I_{rel} (%)): 312 $[M]^+$ (36), 221 $[M - PhCH_2]^+$ (12), 121 $[Ph(CO)O]^+$ (94), 91 $[PhCH_2]^+$ (100).

1-[2-(*tert*-Butyldimethylsilyloxy)phenyl]-3-phenylprop-2-yn-1-one (17c). Yield 2.01 g (80%), oil. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 8.04 (dd, 1 H, J = 7.7 Hz, J = 1.6 Hz); 7.63 (d, 2 H, J = 7.1 Hz); 7.3—7.49 (m, 4 H); 7.08 (t, 1 H, J = 7.5 Hz); 6.93 (d, 1 H, J = 8.2 Hz); 1.07 (s, 9 H); 0.29 (s, 6 H). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 177.8, 156.1, 134.2, 132.9 (2 C); 132.6, 130.4, 129.5, 128.5 (2 C); 121.5, 121.0, 120.6, 91.4, 88.8, 25.8 (3 C); 18.4, −4.1 (2 C). MS, m/z (I_{rel} (%)): 336 $[M]^+$ (5), 321 $[M - Me]^+$ (14), 279 $[M - Bu^t]^+$ (83), 249 $[M - Bu^t - 2\ Me]^+$ (37), 221 $[M - C_6H_{14}Si]^+$ (7), 159 $[C_6H_{14}SiOCHCH_2]^+$ (100).

2,3-Dibromo-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (8). A solution of 1-(2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**6**) (0.3 g, 1.35 mmol) in dichloroethane was stirred with bromine (0.23 g, 1.45 mmol) at room temperature for 8 h (monitoring by TLC). The solvent was removed, and the residue was purified by column chromatography with light petroleum as an eluent. Yield 46%, m.p. 136—138 °C. ^{1}H NMR ($CDCl_3$), δ: 11.44 (s, 1 H_{OH}); 7.78 (d, 1 H, J = 8.1 Hz); 7.55—7.68 (m, 3 H); 7.41—7.52 (m, 3 H); 7.11 (d, 1 H_{CHCOH}, J = 8.4 Hz); 7.11 (t, 1 H, J = 7.6 Hz). MS, m/z (I_{rel} (%)): 380 $[M]^+$ (9), 302 $[M - Br]^+$ (68), 221 $[M - 2\ Br]^+$ (40), 194 $[M - Br_2C_2H_2]^+$ (21), 180 $[M - Br_2C_2H_2O]^+$ (15), 165 $[M - Br_2C_2H_2O_2]^+$ (19), 129 $[M - Br_2PhO]^+$ (18), 121 $[Ph(CO)O]^+$ (100), 102 [PhCCH] (35), 93 $[PhO]^+$ (67), 76 $[Ph]^+$ (44). Found (%): C, 47.21; H, 2.72; Br, 41.74. $C_{15}H_{10}Br_2O_2$. Calculated (%): C, 47.16; H, 2.64; Br, 41.83.

1-(2-Hydroxyphenyl)-2,3-diiodo-3-phenylprop-2-en-1-one (9). A solution of 1-(2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**6**) (0.3 g, 1.35 mmol) in diethyl ether was stirred with excess iodine (0.65 g, 2.55 mmol) at room temperature. After completion of the reaction (monitoring by TLC), the solvent was removed and the precipitate that formed was purified by column chromatography with light petroleum as an eluent. Yield 28%, m.p. 167—169 °C. ^{1}H NMR ($CDCl_3$), δ: 11.51 (s, 1 H_{OH}); 7.81 (d, 1 H, J = 8.0 Hz); 7.58 (t, 1 H, J = 7.3 Hz); 7.38—7.51 (m, 5 H); 7.10 (d, 1 H, C<u>H</u>COH, J = 8.4 Hz); 7.11 (t, 1 H, J = 7.6 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 197.1, 164.3, 144.0, 137.6, 132.4, 129.4, 128.7 (2 C); 128.3 (2 C); 119.7, 119.0, 115.0, 97.3, 90.6. MS, m/z (I_{rel} (%)): 476 $[M]^+$ (21), 349 $[M - I]^+$ (30), 253 $[M - PhIO]^+$ (30), 222 $[M - 2\ I]^+$ (40), 194 $[M - I_2C_2H_2]^+$ (14), 129 $[M - I_2PhO]^+$ (30), 121 $[Ph(OH)CO]^+$ (100), 93 $[PhO]^+$ (82), 77 $[Ph]^+$ (16). Found (%): C, 37.90; H, 2.16. $C_{15}H_{10}I_2O_2$. Calculated (%): C, 37.85; H, 2.12.

3-Bromo-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (10). A 48% aqueous solution of HBr (0.2 mL, d = 1.49) was added to a solution of 1-(2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**6**) (0.2 g, 0.9 mmol) in glacial acetic acid. The reaction mixture was stirred at 60 °C until the reaction was completed (monitoring by TLC). The solvent was removed, and the residue was purified by column chromatography with light petroleum as an eluent. Yield 64%, m.p. 82—84 °C. ^{1}H NMR ($CDCl_3$), δ: 12.15 (s, 1 H_{OH}); 7.79 (d, 1 H, J = 8.0 Hz); 7.69—7.75 (m, 2 H); 7.43—7.57 (m, 5 H); 7.05 (d, 1 H, J = 8.4 Hz); 6.93 (t, 1 H, J = 7.6 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 195.5, 163.2, 138.7, 136.7, 134.8, 130.5, 130.4, 128.5 (2 C); 127.9 (2 C); 124.3, 119.8, 118.9, 118.5. MS, m/z (I_{rel} (%)): 302 $[M]^+$ (5), 223 $[M - HBr]^+$ (100), 194

$[M - C_2H_2]^+$ (5), 165 $[M - COH - C_2H_2]^+$ (17), 129 $[M - PhO]^+$ (11), 121 $[Ph(CO)O]^+$ (68), 102 [PhCCH] (33), 93 $[PhO]^+$ (51). Found (%): C, 59.59; H, 3.81; Br, 26.22. $C_{15}H_{11}BrO_2$. Calculated (%): C, 59.43; H, 3.66; Br, 26.36.

3,6-Dibromo-2-phenylchromone (11). Excess bromine was added to a solution of compound **6** (0.1 g, 0.45 mmol) in dry dichloroethane. The reaction mixture was stirred at room temperature until the reaction was completed (monitoring by TLC). The solvent was removed to give product **7** (0.12 g), which was dissolved in ethanol (5 mL). Sodium acetate (0.074 g, 0.92 mmol) was added to the solution. The reaction mixture was refluxed for 1 h and poured into water. The precipitate that formed was filtered off and dissolved in CH_2Cl_2. The resulting solution was passed through a short column with silica gel and concentrated. Yield 61%, m.p. 190 °C (*cf.* Ref. 11: m.p. 190 °C). ^{1}H NMR ($CDCl_3$), δ: 8.4 (d, 1 H, J = 1.8 Hz); 7.78—7.92 (m, 3 H); 7.50—7.64 (m, 3 H); 7.42 (d, 1 H, J = 8.9 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 171.8, 162.1, 154.3, 137.1, 132.4, 131.2, 129.7 (2 C); 128.9, 128.3 (2 C); 122.9, 119.7, 118.9, 109.1. MS, m/z (I_{rel} (%)): 380 $[M]^+$ (100), 301 $[M - Br]^+$ (5), 200 $[BrPh(CO)O]^+$ (46), 91 $[PhO]^+$ (74). Found (%): C, 47.46; H, 2.20; Br, 42.23. $C_{15}H_8Br_2O_2$. Calculated (%): C, 47.41; H, 2.12; Br, 42.05.

3-Bromo-2-phenylchromone (12). A mixture of compound **8** (0.07 g, 0.183 mmol) and excess NaOAc (0.045 g, 0.55 mmol) was refluxed in ethanol for 4 h (monitoring by TLC) and then poured into water. The precipitate that formed was filtered off and dissolved in CH_2Cl_2. The resulting solution was passed through a short column with silica gel and concentrated. Yield 0.041 g (74%), m.p. 119—120 °C (*cf.* Ref. 12: m.p. 124—125 °C). ^{1}H NMR ($CDCl_3$), δ: 8.32 (d, 1 H, J = 7.7 Hz); 7.82—7.96 (m, 2 H); 7.74 (t, 1 H, J = 7.4 Hz); 7.41—7.64 (m, 5 H). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 167.9, 156.8, 150.5, 128.9, 127.7, 125.9, 124.1 (2 C); 123.1 (2 C); 121.4, 120.6, 116.6, 112.7, 104.1. MS, m/z (I_{rel} (%)): 300 $[M]^+$ (33), 300 $[M - H]^+$ (77), 274 $[M - C_2H_2]^+$ (29), 221 $[M - Br]^+$ (33), 180 $[M - BrC_2H_2O]^+$ (14), 165 $[M - BrC_2H_2O_2]^+$ (13), 137 $[M - BrC_4H_4O_2]$ (24), 121 $[Ph(CO)O]^+$ (100), 101 $[PhCO]^+$ (23), 92 $[PhO]^+$ (72), 74 $[C_6H_4]^+$ (67). Found (%): C, 59.85; H, 3.03; Br, 26.59. $C_{15}H_9BrO_2$. Calculated (%): C, 59.83; H, 3.01; Br, 26.53.

2-Phenylchromone (13). Compound **9** (0.074 g, 0.15 mmol) was dissolved in dry DMF (1 mL). Then K_2CO_3 (0.0083 g, 0.6 mmol) was added, and the reaction mixture was stirred at 60 °C for 1 h and poured into water. The precipitate that formed was filtered off and dissolved in CH_2Cl_2. The resulting solution was passed through a short column with silica gel and concentrated. Yield 39%, m.p. 98—99 °C (*cf.* Ref. 13: m.p. 97—99 °C).

2-(3-Bromo-3-phenylprop-2-enoyl)phenyl acetate (14). Compound **10** (0.05 g, 0.165 mmol) was heated in acetic anhydride in the presence of HBr until the reaction was completed (monitoring by TLC). The reaction mixture was poured into water. The product was extracted with CH_2Cl_2 and purified by column chromatography. Yield 0.034 g (61%), m.p. 68—70 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 7.82 (d, 1 H, J = 6.9 Hz); 7.71 (s, 2 H); 7.57 (t, 1 H, J = 6.5 Hz); 7.33—7.46 (m, 5 H); 7.17 (d, 1 H, J = 7.3 Hz); 2.26 (s, 3 H). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 189.4, 169.4, 149.1, 138.9, 134.4, 133.7, 131.4, 130.5, 130.1, 128.7 (2 C); 128.1 (2 C); 127.2, 126.2, 123.8, 121.1. MS, m/z (I_{rel} (%)): 345 $[M]^+$ (5), 265 $[M - Br]^+$ (68), 223 $[M - Br - COMe)]^+$ (84), 165 $[Ph(CO)OCOMe]^+$ (43), 120 $[Ph(CO)O]^+$ (100), 92 $[PhO]^+$ (76), 77 $[Ph]^+$ (43). Found (%): C, 59.23; H, 3.89; Br, 23.30. $C_{17}H_{13}BrO_3$. Calculated (%): C, 59.15; H, 3.80; Br, 23.15.

Synthesis of 3-mercapto-3-phenylprop-2-en-1-ones (general procedure). Thioacetic acid (1.6 mL, 1.71 g, 22.4 mmol) was stirred with Bu^tOK (0.3 g, 2.38 mmol) for 20 min. Then an appropriate phenylpropynone **17a—c** (1.19 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and poured into water. The product from the aqueous layer was extracted with ethyl acetate. The extract was concentrated and passed through a short column with silica gel. Elution with light petroleum gave a dark cherry oily liquid.

3-Mercapto-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one (18a). Yield 59%. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 15.92 (s, 1 H_{SH}); 7.93 (dd, 1 H, J = 1.5 Hz, J = 7.8 Hz); 7.83 (d, 2 H, J = 7.8 Hz); 7.74 (s, 1 H); 7.41—7.53 (m, 4 H); 7.09 (t, 1 H, J = 7.6 Hz); 7.03 (d, 1 H, J = 8.3 Hz); 3.95 (s, 3 H). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 200.4 (C=O); 179.6, 158.1, 145.4, 133.3, 130.8, 130.5, 128.4 (2 C); 126.9 (2 C); 125.5, 120.9, 116.2, 111.9, 55.9. MS, m/z (I_{rel} (%)): 270 $[M]^+$ (29), 239 $[M - MeO]^+$ (68), 135 $[Ph(CS)CH_2]^+$ (92), 120 $[Ph(CO)O]^+$ (51). Found (%): C, 70.79; H, 5.05. $C_{16}H_{14}O_2S$. Calculated (%): C, 71.08; H, 5.22.

1-(2-Benzyloxyphenyl)-3-mercapto-3-phenylprop-2-en-1-one (18b). Yield 68%. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 15.36 (s, 1 H_{SH}); 8.06 (d, 1 H, J = 8.1 Hz); 7.79 (s, 1 H); 7.11—7.54 (m, 13 H); 5.20 (s, 2 H). MS, m/z (I_{rel} (%): 345 $[M]^+$ (37), 255 $[M - PhCH_2OCCH]^+$ (100), 121 $[Ph(CO)OH]^+$ (74). Found (%): C, 75.98; H, 5.12. $C_{22}H_{18}O_2S$. Calculated (%): C, 76.27; H, 5.24.

1-[2-(*tert*-Butyldimethylsilyloxy)phenyl]-3-mercapto-3-phenylprop-2-en-1-one (18c). Yield 84%. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 14.86 (s, 1 H_{SH}); 7.72—7.84 (m, 3 H); 7.32—7.57 (m, 5 H); 7.01—7.12 (m, 1 H); 6.82—6.99 (m, 1 H); 0.88 (s, 9 H); 0.24 (s, 6 H). MS, m/z (I_{rel} (%)): 370 $[M]^+$ (48), 355 $[M - Me]^+$ (68), 313 $[M - Bu^t]^+$ (98), 255 $[M - SiMe_2Bu^t]^+$ (12), 135 $[Ph(CS)CH_2]^+$ (86), 120 $[Ph(CO)O]^+$ (100). Found (%): C, 67.83; H, 6.98. $C_{21}H_{26}O_2SiS$. Calculated (%): C, 68.06; H, 7.07.

References

1. L. Carlsen, F. Duus, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1768.
2. A. Gorski, Y. Posokhov, B. K. V. Hansen, J. Spanget-Larsen, J. Jasny, F. Duus, P. E. Hansen, J. Waluk, *Chem. Phys.*, 2006, **328**, 205.
3. R. M. Claramunt, C. López, M. D. Santa María, D. Sanz, J. Elguero, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2006, **49**,169.
4. Y. Posokhov, A. Gorski, J. Spanget-Larsen, F. Duus, P. E. Hansen, J. Waluk, *Chem. Phys. Lett.*, 2001, **350**, 502.
5. T. Honjo, H. Freiser, *Anal. Chem.*, 1981, **53**, 1258.
6. B. Andresen, F. Duus, S. Bolvig, P. E. Hansen, *J. Mol. Struct.*, 2000, **552**, 45.
7. R. T. LaLonde, *J. Chem. Soc., Chem. Commun.*, 1982, 401.
8. H. Harkat, A. Blanc, J.-M. Weibel, P. Pale, *J. Org. Chem.*, 2008, **73**, 1620.
9. M. Yoshida, Y. Fujino, T. Doi, *Org. Lett.*, 2011, **13**, 4526.
10. C. Zhou, A. V. Dubrovsky, R. C. Larock, *J. Org. Chem.*, 2006, **71**, 1626.
11. M. Hoshino, *Nippon Kagaku Zasshi*, 1957, **78**, 1754.
12. K. Jakhar, J. K. Makrandi, *Indian J. Chem., Sect. B*, 2012, **51**, 770.

Received February 11, 2013;
in revised form March 14, 2013